

Capability of the free-ion eigenstates for crystal-field splitting

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Abstract

Any electron eigenstate $|\Psi\rangle$ of the paramagnetic ion open-shell is characterized by the three independent multipole asphericities $A_k = \langle \Psi | |C^{(k)}| | \Psi \rangle$ for $k = 2, 4$ and 6 related to the second moments of the relevant crystal-field splittings by $\sigma_k^2 = [1/(2J+1)] A_k^2 S_k^2$, where $S_k^2 = [1/(2k+1)] \sum_q |B_{kq}|^2$. The A_k can serve as a reliable measure of the state $|\Psi\rangle$ capability for the splitting produced by the k -rank component of the crystal-field Hamiltonian and allow one to verify any fitted crystal-field parameter set directly comparing the calculated and the experimental second moments of the relevant crystal-field splittings. We present the multipole characteristics A_k for the extensive set of eigenstates from the lower parts of energy spectra of the tripositive $4f^N$ ions applying in the calculations the advanced eigenfunctions of the free lanthanide ions obtained based on the M. Reid f -shell programs. Such amended asphericities are compared with those achieved for the simplified Russell-Saunders states. Next, they are classified with respect to the absolute or relative weight of the A_k in the multipole structure of the considered states. For the majority of the analyzed states (about 80%) the A_k variation is of order of only a few percent. Some essential changes are found primarily for several states of Tm^{3+} , Er^{3+} , Nd^{3+} , and Pr^{3+} ions. The detailed mechanisms of such A_k changes are unveiled. Particularly, certain noteworthy cancelations as well as enhancements of their magnitudes are explained.

PACS: 71.15.-m, 71.23.An, 71.70.Ch, 75.10.Dg

1. Introduction

The spherical harmonic operators $C_q^{(k)}$ in the one-electron crystal-field (CF) Hamiltonian $\mathcal{H}_{CF} = \sum_i \sum_{k,q} B_{kq} C_q^{(k)}(\vartheta_i, \varphi_i)$ [1], written shortly as $\mathcal{H}_{CF} = \sum_{k,q} B_{kq} C_q^{(k)}$, act on the angle coordinates ϑ_i, φ_i of individual unpaired electrons (i) of the central ion in its initial eigenstates $|\Psi\rangle$ that are superpositions of the Russel-Saunders (RS) states $|l^N SLJM_J\rangle$. The B_{kq} stand for the crystal-field parameters (CFP) for the above specified operators. For complex many-electron states the one-electron character of the $C_q^{(k)}$ operators manifests itself by the 6- j symbols in their developed matrix elements [1-5] and the

doubly reduced matrix elements of the unit tensor operator $U^{(k)}$ [1-5] (Section 2, Eq.(2)). They both reveal a decomposition of the coupled many-electron state into its one-electron spinorbitals. Thus, any matrix element $\langle \Psi | C_q^{(k)} | \Psi \rangle$ is concerned exclusively with the intrinsic properties of the central ion electron eigenstate $|\Psi\rangle$. The reduced (double bar) matrix elements is defined by [1-5]

$$\langle l^N SLJ || C^{(k)} || l^N SL' J' \rangle = (-1)^{J-M_J} \begin{pmatrix} J & k & J' \\ -M_J & q & M_{J'} \end{pmatrix}^{-1} \langle l^N SLJM_J | C_q^{(k)} | l^N SL' J' M_{J'} \rangle, \quad (1)$$

where the factor preceding the matrix element is the reciprocal of the 3- j symbol [1-5]. The reduced matrix element is independent of the reference frame orientation and hence also of M_J . The diagonal reduced elements $\langle \Psi || C^{(k)} || \Psi \rangle$ represent the 2^k -pole asphericities A_k (for $k = 2, 4$ and 6) of the considered electron state $|\Psi\rangle$ [6] and these dimensionless values can serve as a reliable measure of the state capability for CF splitting by the k -rank CF Hamiltonian (Section 3). The electron density distribution of the f -electron states is fully described by the first three multipoles with even $k = 2, 4$ and 6 . The asphericities A_k for 105 lower lying electron eigenstates of all the trivalent lanthanide ions are compiled in Table 1 (Section 2). They have been calculated for the corrected eigenstates including J -mixing effect [7] and the outstanding set of the free-ion data [8] and subsequently compared with those corresponding to the one-component RS states [6]. The A_k magnitudes and their possible variations due to the J -mixing of the RS states are thoroughly discussed. An inseparable entanglement of the asphericities A_k and the k -components of the CF strength S_k [9-12] seen in the expression for the second moment of the splitting σ_k [10, 13, 14] (Section 3) justifies the A_k as a reliable capability of the relevant state for the $2^{(k)}$ -pole partial CF splitting. By the fundamental law of additivity $\sigma^2 = \sum_k \sigma_k^2$ [10, 13, 14], resulting from the orthogonality of the 3- j symbols [3,4] (Eq.(1)), the global σ^2 can be expressed by means of the A_k and S_k components. Tables 2-6 show the classification of the examined eigenstates with respect to their multipole structure (Section 4). The states distinguished by the strongest and the weakest $A = (A_2^2 + A_4^2 + A_6^2)^{1/2}$, by the strongest and the weakest $|A_k|$, and finally those with the largest and the smallest $|A_k|/A$ for $k = 2, 4$ and 6 have been selected respectively. In turn, Section 5 gives a few instructive examples unveiling the mechanisms of the A_k changes induced by the J -mixing of the RS states. A special attention has been paid to the strong enhancements and cancelations among the asphericities A_k .

2. Multipole characteristics of the $4f^N$ tripositive free-ion eigenstates including J -mixing effects

The k -rank multipole moment of an electron eigenstate $|\Psi\rangle$ which is a superposition of the RS states with various L and S but the same J can be evaluated based on the reduced matrix element $\langle \Psi || C^{(k)} || \Psi \rangle$ of the respective k -rank spherical harmonic operator. According to the Wigner-Eckart theorem [5,15] such quantity is independent of the reference frame orientation and adequately expresses the 2^k -pole type asphericity of the given eigenstate $|\Psi\rangle$. For the spherical electron density distribution the matrix element identically vanishes for $k = 2, 4$ and 6 . It plays also a crucial role as a scaling factor in the CF Hamiltonian interaction matrices and hence participates in both the calculational and fitting CFP procedures. In the case of J -mixing approach, i.e. for fixed J , the reduced matrix element can be expressed by the sum of all diagonal and off-diagonal matrix elements occurring in the $\langle \Psi || C^{(k)} || \Psi \rangle$ expansion [1,5,16]

$$\langle l^N SLJ || C^{(k)} || l^N SL' J \rangle = (-1)^{S+L'+J+k} (2J+1) \left\{ \begin{matrix} J & J & k \\ L' & L & S \end{matrix} \right\} \langle l^N SL || U^{(k)} || l^N SL' \rangle \langle l || C^{(k)} || l \rangle, \quad (2)$$

where the first factor on the right side defining the sign of the reduced element depends on the parity of the sum of four numbers, in principle autonomous, what leads to the sign randomness. The second

factor stands for the degeneracy of the state, the third one is the 6-j symbol revealing what part of the final $|SLJ\rangle$ function belongs to the orbital part $|SL'\rangle$ [17]. Finally, the double-bar matrix element of the unit tensor operator $U^{(k)}$ depends how N one-electron angular momenta \vec{l} of the l^N configuration couple into the resultant \vec{L} [18]. The one-electron reduced matrix element $\langle l||C^{(k)}||l\rangle$ for $l = 3$ is equal to -1.3663 , 1.1282 and -1.2774 for $k = 2, 4$ and 6 , respectively.

The M_J quantum numbers and the q index do not appear in Eq.(2) (compare with Eq.(1)). It clearly shows that the reduced matrix elements and in consequence the A_k are independent of the reference frame choice. Any element of the $\langle\Psi||C^{(k)}||\Psi\rangle$ expansion encloses additionally the product of amplitudes of the two involved components in the $|\Psi\rangle$ superposition together with their signs. The reduced matrix element (Eq.(2)) differs from zero only for the same S quantum number (in the bra and ket) since the $C^{(k)}$ acts exclusively on the configurational coordinates of the electrons, and for the same parity of L and L' . These requirements reduce the number of the non-zero off-diagonal matrix elements between various components of the J -mixed eigenfunctions.

Such multipole characteristics have been evaluated earlier for the pure (one-component) RS open-shell electron eigenstates [6]. In Table 1 we compare them with the corrected characteristics for the $4f^N$ tripositive ion eigenstates obtained in the more accurate J -mixing approach based on the M. Reid f -shell programs [7] and the free-ion data reported by Carnall et al [8]. In the considered J -mixed superpositions the average number of RS components amounts to 7, whereas the average number of the constituent matrix elements 13. In turn, the maximal number of the components reaches 22, whereas the maximal number of the matrix elements amounts to 64 (including 42 off-diagonal ones) what occurs for the ninth eigenstate of Dy^{3+} ion (No.70 in Table 1) with $|^6F_{7/2}\rangle$ state as the upper component.

In total, we have taken into account 105 lower lying eigenstates of the three-valent RE ions from Ce^{3+} ($4f^1$) up to Yb^{3+} ($4f^{13}$). Table 1 covers also the basic attributes of the considered eigenstates: the upper RS component, its amplitude in the normalized superposition, the consecutive number in the ion's spectrum [7], the eigenenergy in cm^{-1} , and the number of components with the amplitude exceeding 0.01. The number in the first column of Table 1 identifies any quoted state or its parameters consistently throughout the whole paper. It is instructive to compare the asphericities of the pure RS states [6] with those of the corrected J -mixed eigenstates. It turns out that from among the 105 analysed states only about 20% of them differ markedly in the asphericities from their RS counterparts, i.e. their upper states. Primarily, these are the states of the following ions: Tm^{3+} ($4f^{12}$), Er^{3+} ($4f^{11}$), Nd^{3+} ($4f^3$), and Pr^{3+} ($4f^2$) (Table 1). By sheer coincidence two various states of Tm^{3+} ion: No.99 and No.103 are characterized by the same dominating component $|^3P_2\rangle$, but it does not lead to any misunderstanding because we do not use this ambiguous state description.

There exist the following J -mixing mechanisms that produce the observed changes in the asphericity of the states. Firstly, the normalization of any superposition of states reduces naturally the upper state amplitude, whereas its square determines the upper state asphericity input. Secondly, additional diagonal and off-diagonal terms in the the matrix element $\langle\Psi||C^{(k)}||\Psi\rangle$ expansion differ in magnitudes and signs. The sign of each individual diagonal term is specified exclusively by the sign of the respective A_k on the involved component. Its magnitude, however, comes from the product of the $|A_k|$ and the square of the component amplitude in the superposition. In turn, any off-diagonal term is a product of 6 factors including two involved amplitudes (Eq.(2)). Its sign results from the product of 6 signs, in principle autonomous. To cope with this matter effectively one should consider all the additional diagonal and off-diagonal contributions along with their various possible magnitudes and signs. Based on these investigations four types of the resultant A_k modifications can be noticed in Table 1:

- (i) Due to insignificant J -mixing admixtures to the upper state only small changes (within a few percent) arise in the pertinent $|A_k|$, which are the algebraic sum of the normalization effect and the additional diagonal and off-diagonal corrections. Such effect occurs for about 80% of the states presented in Table 1. However, the proximity of the A_k for the RS and the corrected J -mixed

states can be also accidental. By way of example, for eigenstate No.28 of Nd^{3+} ion the upper state $|^3P_{3/2}\rangle$ amplitude reaches merely 0.7205 and its contribution to the A_2 of the superposition only $(0.7205)^2(0.2981) = 0.1548$. Nevertheless, the remaining diagonal (0.2128) and off-diagonal (-0.0858) inputs, relatively large, lead in sum to the $A_2 = 0.2818$ that accidentally is close to 0.2981, which is the value for the $|^3P_{3/2}\rangle$ state.

- (ii) The sum of the corrections is substantial with respect to the upper state A_k and has the same sign as the A_k . Here an enhancement of the $|A_k|$ occurs. Such resultant effect is observed for the states No.: 27, 88, 97, 98, and 103 in the case of A_2 , for the states No.: 8, 64, 65, and 93 in the case of A_4 , and for the state No.95 in the case of A_6 .
- (iii) The sum of the corrections is substantial but with the opposite sign than that of the upper state A_k . In this case a partial compensation of the $|A_k|$ (including the complete one) or even the sign conversion of A_k takes place. Such result has been found in the case of A_2 for the states No.: 8, 9, 21, 24, 25, 79, 84, 85, 86, 93, 95, 99, in the case of A_4 for the states No.: 9, 10, 21, 24, 25, 85, 86, 88, 95, 97, 98, and in the case of A_6 for the states No.: 3, 8, 9, 21, 24, 25, 27, 64, 65, 79, 84, 85, 86, 88, 93, 98.
- (iv) The corrections generate the only contribution to A_k that for the initial state is equal to zero. It takes place for the states No.14 (A_4), No.23 (A_2), No.80 (A_2, A_4), No.87 (A_2), No.99 (A_4), No.103 (A_4).

The detailed mechanisms of the asphericity modifications induced by the J -mixing effect will be thoroughly analyzed for some representative examples in Section 5.

3. The asphericity of an electron eigenstate and its crystal-field splitting

The asphericity A_k for $k = 2, 4$ and 6 of any electron state may serve as a reliable measure of its capability for CF splitting produced by the $\mathcal{H}_{CF}^{(k)}$ - the k -th component of the \mathcal{H}_{CF} . It stems from the fundamental relationship between the CF splitting second moment σ_k and the A_k [10,13,14]

$$\sigma_k^2 = [1/(2J+1)] A_k^2 S_k^2, \quad (3)$$

where $S_k^2 = [1/(2k+1)] \sum_q |B_{kq}|^2$ is the square of the CF strength of the 2^k -pole \mathcal{H}_{CF} component [9-12], and $(2J+1)$ is the degeneracy of the given state with a good quantum number J . In fact, the above relationship (Eq.(3)) implies from the spherical harmonic addition theorem [19] concerning the expansion of $1/r_{ij}$ into the series of $C_q^{(k)}(\vartheta_i, \varphi_i) \cdot C_q^{(k)*}(\theta_j, \phi_j)$ components. They are the products of the conjugated spherical harmonics defined for the separated indices i and j . In the CF context the first factor refers to the electron density angle distribution of the central ion unperturbed eigenstate, whereas the second refers to the surrounding charges. In fact, this separation lies in the background of the whole formalism.

As is seen from Eq.(3) the asphericity A_k can be treated as a potential capability of the considered state for the 2^k -pole CF splitting since the second factor S_k represents a separate and unrelated external impact. The A_k can be either positive or negative (Section 2) what symbolically may be imagined as asphericities of convex or concave type. The A_k sign is irrelevant for the σ_k , but is crucial calculating the resultant asphericities of the superposition of states.

The question arises how the global second moment σ can be expressed by means of the asphericities of the involved electron eigenstate. As is known, the square of the global second moment σ^2 is a simple sum of the second moment squares of the individual components.

$$\sigma^2 = [1/(2J+1)] (A_2^2 S_2^2 + A_4^2 S_4^2 + A_6^2 S_6^2). \quad (4)$$

To describe σ^2 it is convenient to introduce two auxiliary and figurative vectors: $\mathcal{A}(A_2^2, A_4^2, A_6^2)$ and $\mathcal{S}(S_2^2, S_4^2, S_6^2)$ within the three-dimensional orthogonal reference frame based on the A_k^2 (or S_k^2) axes. Then, $\sigma^2 = [1/(2J+1)] \mathcal{A} \cdot \mathcal{S}$ is defined by their scalar product. All the components of the \mathcal{A} and \mathcal{S} vectors are positive by definition and can be expressed by the spherical angle coordinates only within the ranges of $0 \leq \theta \leq \pi/2$ and $0 \leq \phi \leq \pi/2$. Eq.(4) shows that the CF splitting is determined by the two inseparable independent quantities A_k and S_k mutually entangled. The figurative vectors \mathcal{A} and \mathcal{S} may be orthogonal, what happens when both the vectors lie either on the two frame axes or one of them lies along an axis whereas the second belongs to the perpendicular plane. Then, always $\sigma^2 = 0$ in spite of some non-zero A_k and S_k . Simultaneously, Eq.(4) enables us to critically verify the meaning of such quantities like $S = (\sum_k S_k^2)^{1/2}$ and $A = (\sum_k A_k^2)^{1/2}$ [6]. In general, no apparent physical sense can be assigned to them.

4. The range of capability of the $4f^N$ tripositive free ion eigenstates for crystal-field splitting

Similarly to the approximated RS states $|^{2S+1}L_J\rangle$ of triply ionized lanthanides [6], the eigenstates amended by the J -mixing [7] are characterized by an exceedingly diversified multipole structure both in qualitative and quantitative way (Table 1). Such random to a large extent diversity stems from a stochastic character with respect to the magnitude and sign of the multifactorial expression for the $C^{(k)}$ operator reduced matrix element (Eq.(2)). The chaotic dispersion of the A_k magnitudes and signs is well exhibited in Tables 2-6 by the eigenstates chosen from among all the 105 studied ones: the top ten states of the strongest or weakest $A = (A_2^2 + A_4^2 + A_6^2)^{1/2}$ (Table 2), the ten ones of the strongest $|A_k|$ (Tables 3), the ten of the weakest $|A_k|$ (Table 4), and finally the ten states of the highest $|A_k|/A$ (Table 5), as well as the ten ones of the lowest $|A_k|/A$ (Table 6). The $|A_k|/A$, which is a cosine of the angle between the (A_2, A_4, A_6) vector and the distinguished axis representing the A_k , gives the relative weight of the chosen 2^k -pole in the eigenstate multipole structure. It is enough to notice that A takes values from 0 to 3.3784, whereas the entirely independent one of another $|A_k|$ change within the ranges: $0 < |A_2| \leq 3.0273$, $0 < |A_4| \leq 1.4303$, and $0 < |A_6| \leq 1.7765$. In consequence, the multipole structure of the considered states is widely differentiated and can assume also the forms with only one prevailing multipole. For example, No.14 eigenstate $|^3P_2\rangle$ of Pr^{3+} ion is characterized by the predominating role of the 2^2 -pole component ($|A_2|/A = 0.9917$), No.43 eigenstate $|^6F_{5/2}\rangle$ of Sm^{3+} ion by the 2^4 -pole component ($|A_4|/A \simeq 1.0000$), and No.18 eigenstate $|^4I_{15/2}\rangle$ of Nd^{3+} ion by the prevailing 2^6 -pole component ($|A_6|/A = 0.8812$), however not so distinctly as in the two previous cases.

The highest total asphericities (the top A values), it means the strongest total capabilities for the CF splitting, are found in the states with large L (and J) quantum numbers (Table 2). Such states are weakly disturbed by the J -mixing interaction due to a small number of the partner RS states of the same J and large energy gaps between them. Their calculated asphericities are close to those for the relevant upper states. On the contrary, the eigenstates with the weakest asphericities have quite often their A_k significantly changed with respect to those for their RS counterparts. In general, it results from a similar level of the J -mixing corrections in both the cases, and a substantial difference in their initial magnitudes.

Tables 1-6 enable to note an evident correspondence between the calculated A_k for the pairs of the lanthanide ions with the complementary electron configurations $4f^N$ and $4f^{14-N}$: (Ce^{3+} , Yb^{3+}), (Pr^{3+} , Tm^{3+}), (Nd^{3+} , Er^{3+}), (Pm^{3+} , Ho^{3+}), (Sm^{3+} , Dy^{3+}) and (Eu^{3+} , Tb^{3+}). The opposite A_k sign of the pair-partners results from the opposite sign of the related matrix elements of the $U^{(k)}$ operators [18], and is mainly a repercussion of the Hund's rules governing the eigenstates sequence, it means their location in the free-ion energy spectrum. As a good example of such case may serve the difference between the bottom parts of the energy diagrams of Pr^{3+} and Tm^{3+} ions. In the energy spectrum of

Pr^{3+} ion the RS states $|^3H_4\rangle$ and $|^3F_4\rangle$ interacting via J -mixing are located one to another as far as possible: the $|^3H_4\rangle$ is the lowest state of the term 3H , whereas the $|^3F_4\rangle$ the highest one of the term 3F . In Tm^{3+} ion, in the reverse order, the $|^3H_4\rangle$ is the highest state of the 3H term, whereas the $|^3F_4\rangle$ the lowest state of the term 3F . In fact, the $|^3F_4\rangle$ state lies below the state $|^3H_4\rangle$ [16]. The energy gap between the states $|^3H_4\rangle$ and $|^3F_4\rangle$, their so-called energy denominator, determines the efficiency of the J -mixing interaction.

5. Discussion

The calculated asphericities $A_k = \langle \Psi | C^{(k)} | \Psi \rangle$ of the trivalent $4f^N$ ions are not the actual ones due to approximate nature of the applied eigenfunctions $|\Psi\rangle$, but their reliability can be improved replacing the initial functions (e.g. those of the RS type) by their various superpositions. In the case of simultaneous diagonalisation of the interaction matrix including the Coulomb repulsion and the spin-orbit coupling these are the superpositions of the RS functions with the same J but different L and S quantum numbers [7]. The A_k variations seen in Table 1 are limited mainly by the scale of the component admixtures. Additional role play the magnitudes of the relevant diagonal and off-diagonal matrix elements of the $C^{(k)}$ operator within the superposition, as well as the mutual competition between the corrections. In most cases the amplitudes of the admixtures are rather small. Therefore, for the majority of the lower lying eigenstates (about 80%) of the trivalent lanthanide ions there appear only inconsiderable differences between the A_k calculated for the model RS states [6] and those including their J -mixing (Table 1). Nevertheless, for certain part of the eigenstates, particularly the excited ones, the observed changes become essential, indeed. They illustrate well the types of the resultant J -mixing effects mentioned in Section 2. Some instructive mechanisms leading to such variations are analyzed in details below for several chosen examples.

Let us consider No.8 eigenstate in Table 1. It is the sixth state of Pr^{3+} ion of the composition: $0.8087|^3F_4\rangle + 0.1225|^3H_4\rangle - 0.5753|^1G_4\rangle$ with the dominating $|^3F_4\rangle$ component. The diagonal contributions to the A_2 amount to: $(0.8087)^2(0.4672) = 0.3778$, $(0.1225)^2(-1.2367) = -0.0186$, $(-0.5753)^2(-0.3058) = -0.1012$, and the only off-diagonal input $\langle (0.8087)^3F_4 | C^{(2)} | (0.1225)^3H_4 \rangle = -0.0141$. The accumulation of the three negative corrections reduces the A_2 from 0.4672 down to 0.2439. The diagonal contributions to the A_4 are negative and reach: $(0.8087)^2(-0.2906) = -0.1901$, $(0.1225)^2(-0.7395) = -0.0111$, $(-0.5753)^2(-1.2150) = -0.4021$, and the off-diagonal element $\langle (0.8087)^3F_4 | C^{(4)} | (0.1225)^3H_4 \rangle = 0.0549$. Here, the strong diagonal input of the $|^1G_4\rangle$ governs the magnitude and sign of the $A_4 = -0.2906$. In turn, the diagonal contributions to the A_6 are equal to: $(0.8087)^2(0.1558) = 0.1019$, $(0.1225)^2(0.7706) = 0.0116$, $(-0.5753)^2(-1.5299) = -0.5064$, and the off-diagonal one $\langle (0.8087)^3F_4 | C^{(6)} | (0.1225)^3H_4 \rangle = 0.1649$. Again, as above, the diagonal negative input of the $|^1G_4\rangle$ dominates and the ultimate $A_6 = -0.2280$ results from a partial compensation of all the contributions.

Eigenstate No.21, the seventh state of Nd^{3+} ion, is composed of $-0.3700|^4F_{9/2}\rangle - 0.1458|^4G_{9/2}\rangle + 0.1525|^4I_{9/2}\rangle + 0.3381|^2G(1)_{9/2}\rangle - 0.2799|^2G(2)_{9/2}\rangle - 0.2805|^2H(1)_{9/2}\rangle + 0.7398|^2H(2)_{9/2}\rangle$ with the prevailing $|^2H(2)_{9/2}\rangle$ state. All the weak diagonal contributions to the A_2 are almost compensated achieving in sum 0.0092 with respect to the dominating state input $(0.7398)^2(-0.0069) = -0.0038$. The decisive are the positive off-diagonal terms $\langle (0.3381)^2G(1)_{9/2} | C^{(2)} | (-0.2799)^2G(2)_{9/2} \rangle = 0.1655$, and $\langle (0.2805)^2H(1)_{9/2} | C^{(2)} | (0.7398)^2H(2)_{9/2} \rangle = 0.1225$, giving finally the $A_2 = 0.2920$. Here, the dominating state input to the A_4 amounts to $(0.7398)^2(0.4816) = 0.2636$ and the sum of all the seven diagonal elements 0.1675 is somewhat less. In this situation the relatively large and negative off-diagonal element $\langle (0.2805)^2H(1)_{9/2} | C^{(4)} | (0.7398)^2H(2)_{9/2} \rangle = -0.2508$ decides both on the magnitude and sign of the $A_4 = -0.0638$. Similarly, for the very small positive sum of the partial diagonal elements (0.0055), the final $A_6 = -0.0732$ is determined by the prevailing, as for the modulus, negative off-diagonal element $\langle (0.2805)^2H(1)_{9/2} | C^{(6)} | (0.7398)^2H(2)_{9/2} \rangle = -0.1010$.

Eigenstate No.25, the eleventh state of the Nd^{3+} , is given by $-0.2407|^4G_{11/2}\rangle + 0.0994|^4I_{11/2}\rangle -$

$0.3573|^2H(1)_{11/2}\rangle + 0.8955|^2H(2)_{11/2}\rangle - 0.0515|^2I_{11/2}\rangle$ with the dominating $|^2H(2)_{11/2}\rangle$ component. The sum of the diagonal contributions to the A_2 is -0.0740, including the input -0.0632 from the $|^2H(1)_{11/2}\rangle$. The resultant $A_2 = 0.1289$ is the outcome of mutual competition of the positive off-diagonal term $\langle(-0.3573) \ ^2H(1)_{11/2}||C^{(2)}||(0.8955) \ ^2H(2)_{11/2}\rangle = 0.2080$ and the negative diagonal contribution coming mainly from the state $|^2H(1)_{11/2}\rangle$. The sum of the diagonal elements combining to the A_4 amounts to 0.4454 and is close to the contribution of the dominating $|^2H(2)_{11/2}\rangle$ state, i.e. $(0.8955)^2(0.5373) = 0.4309$. However, it is practically entirely compensated ($A_4 = 0.0001$) by the sum of two negative off-diagonal elements: $\langle(-0.3573) \ ^2H(1)_{11/2}||C^{(4)}||(0.8955) \ ^2H(2)_{11/2}\rangle = -0.4314$ and $\langle(-0.2407) \ ^4G_{11/2}||C^{(4)}||(0.0994) \ ^4I_{11/2}\rangle = -0.0139$. The resultant $A_6 = -0.2027$ is determined by relatively strong off-diagonal input $\langle(-0.3573) \ ^2H(1)_{11/2}||C^{(6)}||(0.8955) \ ^2H(2)_{11/2}\rangle = -0.1791$. All the diagonal elements contribute only -0.0081.

The J -mixing of the RS states can activate some idle states making them susceptible to CF splittings. In other words, they lose their initial effective spherical symmetry. As an example let us examine eigenstate No.87, the sixth state of Er^{3+} ion consisting of $0.8293|^4S_{3/2}\rangle + 0.0443|^4D_{3/2}\rangle + 0.2390|^4F_{3/2}\rangle - 0.4174|^2P_{3/2}\rangle - 0.2797|^2D(1)_{3/2}\rangle - 0.0274|^2D(2)_{3/2}\rangle$. The prevailing element $|^4S_{3/2}\rangle$ is characterized by zero asphericities A_2 , A_4 and A_6 . However, the corrected eigenstate acquires the asphericity $A_2 = -0.1689$ by accumulation of the negative diagonal contributions: $(0.2390)^2(-0.3578) = -0.0204$, $(-0.4174)^2(-0.2981) = -0.0519$, $(-0.2797)^2(-0.5707) = -0.0446$, and the off-diagonal ones: $\langle(0.0443) \ ^4D_{3/2}||C^{(2)}||(0.8293) \ ^4S_{3/2}\rangle = -0.0480$, $\langle(-0.2797) \ ^2D(1)_{3/2}||C^{(2)}||(-0.0274) \ ^2D(2)_{3/2}\rangle = -0.0045$. The states $|^4S_{3/2}\rangle$ and $|^4D_{3/2}\rangle$ do not bring any diagonal inputs, and the state $|^2D(2)_{3/2}\rangle$ gives only 0.0005.

In the case of eigenstate No.3 the ground state of Pr^{3+} ion is given by $0.9856|^3H_4\rangle + 0.1662|^1G_4\rangle - 0.0311|^3F_4\rangle$ and its A_2 and A_4 asphericities change only slightly with respect to the parameters for the pure $|^3H_4\rangle$ state. However, the $|A_6|$ asphericity is noticeably reduced. The diagonal contribution of the $|^1G_4\rangle$ state $(0.1662)^2(-1.5299) = -0.0423$, and the off-diagonal term which is equal to $\langle(0.9856) \ ^3H_4||C^{(6)}||(-0.0311) \ ^3F_4\rangle = -0.0510$ weaken the positive input of the $|^3H_4\rangle$ upper state $(0.9856)^2(0.7706) = 0.7486$ down to the value of 0.6555. It corresponds to attenuation of the state capability for the CF splitting by $\mathcal{H}_{CF}^{(6)}$. An increase in both the $|^3F_4\rangle$ and $|^1G_4\rangle$ admixtures deepen the tendency. It is worth to remember analyzing the CF splitting of the $\text{U}^{4+}(5f^2)$ ion ground state.

As is seen in Eq.(3) the multipole characteristics of the electron eigenstates along with their CF splitting diagrams sheds a new light on the crystal matrix multipole structure and vice versa. Based on the CF splitting diagrams for several electron eigenstates of known multipole characteristics in a specified crystal matrix (with a definite \mathcal{H}_{CF}), as well as the CF splitting diagrams of a specified eigenstate in various CF matrices, we can reconcile the actual A_k for the considered electron states and the S_k for the \mathcal{H}_{CF} s, respectively. A great facilitation in such estimations is an incomplete multipolar structure of the analyzed eigenstates. Such incompleteness may result either from the triangle rule for J , J , k numbers (e.g. for $J = 1, 3/2$ and $k = 4, 6$ or $J = 5/2$ and $k = 6$) or from accidental cancelation of some multipoles due to the J -mixing effect, as it is observed for eigenstates No.25 and No.85 in Table 1. Furthermore, in some CF Hamiltonians the three-component multipole structure is not always complete, like e.g. in the cubic \mathcal{H}_{CF} which is deprived of quadrupolar moment.

The reliable classification of the multipolar structure of both the electron eigenstates and the actual CF Hamiltonians need such kind of comprehensive investigations. The electron eigenstates asphericities A_k allows us to verify the fitted CFP sets comparing the calculated (Eq.(3)) and experimental second moments of the splitting [20]. The fitted CFP sets that well reproduce the experimental spectrum of energy levels for intentionally approximated initial eigenfunctions have by definition an effective character. Therefore, applying the same approximation for all eigenfunctions coming from different energy ranges will undoubtedly lead to errors. Presumably, this is the main reason for difficulties associated with minimization of *rms* deviations in fitted CFP sets. There are some phenomenological attempts to improve the fitting accuracy. In one of them the two-electron correlation CF is introduced

which may be simple expressed by an effective one-electron CF Hamiltonian being dependent on the electron term. In another one the mean k powers of the unpaired electron radii $\langle r^k \rangle$, is made variable with respect to the electron term [5,21,22]. Both the above approaches are formally admissible, but they can be physically ungrounded.

Yet another reflection arises. The dichotomic structure of the CF Hamiltonian [6] and random diversity of the asphericities do not entitle us by no means to exploit the concept of the \mathcal{H}_{CF} multipole series convergence, as the multipole series of an external potential only. The \mathcal{H}_{CF} approximation reducing its multipole structure only to first quadrupolar term is groundless. An exception could be perhaps a unique case when $A_2 = A_4 = A_6$. Obviously, the \mathcal{H}_{CF} three-multipole ($k = 2, 4, 6$) series is a finite one, and not truncated. The higher multipoles do not contribute at all. The second independent factor that controls to a similar extent as the external multipoles the resultant hierarchy of the three CF Hamiltonian terms is the capability A_k of the state for the CF splitting.

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Table 1: Multipole character of the J-mixed electron eigenstates $|\Psi\rangle$ in RE free ions. The eigenfunctions and eigenvalues are calculated using M. Reid f-shell programs [7] and free-ion data reported by Carnall et al [8]. The electron eigenstate data cover respectively: the upper component (Up.Comp.), its amplitude (Ampl.), consecutive no. in the spectrum [7] (no.), energy [cm^{-1}] (E), number of components of amplitude > 0.01 (n). The multipolar asphericities for the upper component of the state are given in the parentheses.

No.	RE ion		Electron eigenstate data					Multipolar asphericity		
	Ion	conf.	Up.Comp.	Ampl.	no.	E	n	$A_2(\Psi)$	$A_4(\Psi)$	$A_6(\Psi)$
1	Ce ³⁺	f^1	$ ^2F_{5/2}\rangle$	1	1	0	1	-1.1711 (-1.1711)	0.7560 (0.7560)	0 (0)
2	Ce ³⁺	f^1	$ ^2F_{7/2}\rangle$	1	2	2750	1	-1.3801 (-1.3801)	0.9670 (0.9670)	-0.3054 (-0.3054)
3	Pr ³⁺	f^2	$ ^3H_4\rangle$	0.9856	1	0	3	-1.2048 (-1.2367)	-0.7693 (-0.7395)	0.6555 (0.7706)
4	Pr ³⁺	f^2	$ ^3H_5\rangle$	1	2	2086	1	-1.3100 (-1.3100)	-0.6833 (-0.6833)	0.4451 (0.4451)
5	Pr ³⁺	f^2	$ ^3H_6\rangle$	0.9985	3	4258	2	-1.5204 (-1.5158)	-0.9511 (-0.9583)	1.1338 (1.1386)
6	Pr ³⁺	f^2	$ ^3F_2\rangle$	0.9880	4	4895	3	0.3400 (0.3187)	-0.0909 (-0.1328)	0 (0)
7	Pr ³⁺	f^2	$ ^3F_3\rangle$	1	5	6284	1	0.3416 (0.3416)	-0.0627 (-0.0627)	-0.3193 (-0.3193)
8	Pr ³⁺	f^2	$ ^3F_4\rangle$	0.8087	6	6718	3	0.2439 (0.4672)	-0.5484 (-0.2906)	-0.2280 (0.1558)
9	Pr ³⁺	f^2	$ ^1G_4\rangle$	0.8009	7	9732	3	-0.0421 (-0.3058)	-0.9275 (-1.2150)	-1.0310 (-1.5299)
10	Pr ³⁺	f^2	$ ^1D_2\rangle$	-0.9430	8	16813	3	0.8354 (0.8765)	0.6203 (0.7968)	0 (0)
11	Pr ³⁺	f^2	$ ^3P_0\rangle$	0.9947	9	20654	2	0 (0)	0 (0)	0 (0)
12	Pr ³⁺	f^2	$ ^3P_1\rangle$	1	10	21274	1	-0.5477 (-0.5477)	0 (0)	0 (0)
13	Pr ³⁺	f^2	$ ^1I_6\rangle$	0.9985	11	21299	2	-3.0273 (-3.0318)	1.4303 (1.4375)	-0.4506 (-0.4554)
14	Pr ³⁺	f^2	$ ^3P_2\rangle$	-0.9549	12	22467	3	0.8563 (0.8366)	0.1112 (0)	0 (0)
15	Nd ³⁺	f^3	$ ^4I_{9/2}\rangle$	0.9844	1	0	5	-0.4758 (-0.4954)	-0.4742 (-0.4904)	-1.0773 (-1.1085)
16	Nd ³⁺	f^3	$ ^4I_{11/2}\rangle$	0.9947	2	1862	4	-0.4978 (-0.5045)	-0.3894 (-0.3935)	-0.3374 (-0.3399)
17	Nd ³⁺	f^3	$ ^4I_{13/2}\rangle$	0.9979	3	3845	3	-0.5615 (-0.5569)	-0.4700 (-0.4691)	-0.6186 (-0.6217)
18	Nd ³⁺	f^3	$ ^4I_{15/2}\rangle$	0.9938	4	5907	2	-0.6587 (-0.6438)	-0.6886 (-0.6850)	-1.7765 (-1.7999)
19	Nd ³⁺	f^3	$ ^4F_{3/2}\rangle$	0.9698	5	11381	6	0.3561 (0.3578)	0 (0)	0 (0)
20	Nd ³⁺	f^3	$ ^4F_{5/2}\rangle$	0.9879	6	12420	6	0.3277 (0.3220)	0.1843 (0.1890)	0 (0)

Table 1 - cont.

No.	RE ion		Electron eigenstate data					Multipolar asphericity		
	Ion	conf.	Up.Comp.	Ampl.	no.	E	n	$A_2(\Psi)$	$A_4(\Psi)$	$A_6(\Psi)$
21	Nd ³⁺	f^3	$ ^2H(2)_{9/2}\rangle$	0.7398	7	12519	7	0.2920 (-0.0069)	-0.0638 (0.4816)	-0.0732 (0.0057)
22	Nd ³⁺	f^3	$ ^4F_{7/2}\rangle$	-0.9648	8	13383	6	0.4650 (0.4601)	0.0533 (0.0537)	-0.4233 (-0.4552)
23	Nd ³⁺	f^3	$ ^4S_{3/2}\rangle$	0.9719	9	13429	5	0.0362 (0)	0 (0)	0 (0)
24	Nd ³⁺	f^3	$ ^4F_{9/2}\rangle$	-0.8670	10	14652	7	0.5748 (0.7136)	-0.3050 (-0.4051)	0.1040 (0.1799)
25	Nd ³⁺	f^3	$ ^2H(2)_{11/2}\rangle$	0.8955	11	15857	5	0.1289 (-0.0076)	0.0001 (0.5373)	-0.2027 (0.0066)
26	Nd ³⁺	f^3	$ ^4G_{5/2}\rangle$	-0.9929	12	17181	5	0.0321 (0.0349)	0.4718 (0.4786)	0 (0)
27	Nd ³⁺	f^3	$ ^4G_{7/2}\rangle$	0.6180	13	17224	6	0.3684 (0.0342)	0.1189 (0.1361)	0.1939 (0.5380)
28	Nd ³⁺	f^3	$ ^2P_{3/2}\rangle$	0.7205	23	26179	6	0.2818 (0.2981)	0 (0)	0 (0)
29	Pm ³⁺	f^4	$ ^5I_4\rangle$	-0.9880	1	0	6	0.4609 (0.4540)	0.4132 (0.4103)	0.7588 (0.7679)
30	Pm ³⁺	f^4	$ ^5I_5\rangle$	-0.9933	2	1255	6	0.4453 (0.4428)	0.2467 (0.2437)	-0.2889 (-0.2958)
31	Pm ³⁺	f^4	$ ^5I_6\rangle$	0.9950	3	2636	8	0.4786 (0.4796)	0.2622 (0.2613)	-0.3007 (-0.3072)
32	Pm ³⁺	f^4	$ ^5I_7\rangle$	-0.9921	4	4102	6	0.5415 (0.5524)	0.3978 (0.4042)	0.2378 (0.2398)
33	Pm ³⁺	f^4	$ ^5I_8\rangle$	-0.9841	5	5625	5	0.6292 (0.6562)	0.6585 (0.6797)	1.6571 (1.7060)
34	Pm ³⁺	f^4	$ ^5F_1\rangle$	0.9798	6	11721	4	-0.2180 (-0.2191)	0 (0)	0 (0)
35	Sm ³⁺	f^5	$ ^6H_{5/2}\rangle$	0.9783	1	0	10	0.8650 (0.8458)	0.2724 (0.2978)	0 (0)
36	Sm ³⁺	f^5	$ ^6H_{7/2}\rangle$	-0.9853	2	1035	9	0.7272 (0.7176)	-0.1291 (-0.1129)	0.6885 (0.7035)
37	Sm ³⁺	f^5	$ ^6H_{9/2}\rangle$	0.9899	3	2243	10	0.7883 (0.7786)	-0.1551 (-0.1423)	0.6503 (0.6845)
38	Sm ³⁺	f^5	$ ^6H_{11/2}\rangle$	-0.9906	4	3571	7	0.9585 (0.9587)	-0.0042 (-0.0108)	0.6924 (0.7152)
39	Sm ³⁺	f^5	$ ^6H_{13/2}\rangle$	-0.9869	5	4978	6	1.2281 (1.2375)	0.3162 (0.3128)	0.4041 (0.4146)
40	Sm ³⁺	f^5	$ ^6F_{1/2}\rangle$	-0.9846	6	6297	7	0 (0)	0 (0)	0 (0)

Table 1 - cont.

No.	RE ion		Electron eigenstate data					Multipolar asphericity		
	Ion	conf.	Up.Comp.	Ampl.	no.	E	n	$A_2(\Psi)$	$A_4(\Psi)$	$A_6(\Psi)$
41	Sm ³⁺	f^5	$ ^6H_{15/2}\rangle$	-0.9782	7	6431	8	1.5794 (1.6095)	0.9086 (0.9134)	-0.8624 (-0.9000)
42	Sm ³⁺	f^5	$ ^6F_{3/2}\rangle$	0.9779	8	6548	10	0.0565 (0.0596)	0 (0)	0 (0)
43	Sm ³⁺	f^5	$ ^6F_{5/2}\rangle$	-0.9719	9	7052	20	0.0033 (0.0130)	-0.1068 (-0.1260)	0 (0)
44	Sm ³⁺	f^5	$ ^6F_{7/2}\rangle$	-0.9752	10	7922	16	-0.1085 (-0.0920)	-0.1612 (-0.2030)	-0.2209 (-0.2276)
45	Sm ³⁺	f^5	$ ^6F_{9/2}\rangle$	0.9824	11	9105	13	-0.2631 (-0.2595)	-0.1020 (-0.1391)	0.2790 (0.2617)
46	Sm ³⁺	f^5	$ ^6F_{11/2}\rangle$	-0.9873	12	10503	6	-0.4884 (-0.4951)	0.2495 (0.2465)	-0.0652 (-0.0853)
47	Eu ³⁺	f^6	$ ^7F_0\rangle$	-0.9663	1	0	6	0 (0)	0 (0)	0 (0)
48	Eu ³⁺	f^6	$ ^7F_1\rangle$	-0.9729	2	382	8	-0.5317 (-0.5477)	0 (0)	0 (0)
49	Eu ³⁺	f^6	$ ^7F_2\rangle$	-0.9809	3	1052	9	-0.4240 (-0.4382)	-0.3961 (-0.3984)	0 (0)
50	Eu ³⁺	f^6	$ ^7F_3\rangle$	0.9867	4	1914	9	-0.2150 (-0.2277)	0.1805 (0.1880)	-0.2154 (-0.2129)
51	Eu ³⁺	f^6	$ ^7F_4\rangle$	-0.9890	5	2898	9	0.1621 (0.1528)	0.5883 (0.6075)	0.7592 (0.7650)
52	Eu ³⁺	f^6	$ ^7F_5\rangle$	-0.9873	6	3957	6	0.7301 (0.7277)	0.4986 (0.5125)	-0.7222 (-0.7419)
53	Eu ³⁺	f^6	$ ^7F_6\rangle$	0.9814	7	5055	8	1.4991 (1.5159)	-0.7080 (-0.7188)	0.2161 (0.2277)
54	Gd ³⁺	f^7	$ ^8S_{7/2}\rangle$	0.9879	1	0	5	0 (0)	0 (0)	0 (0)
55	Tb ³⁺	f^8	$ ^7F_6\rangle$	-0.9793	1	0	9	-1.5028 (-1.5159)	0.7060 (0.7188)	-0.2170 (-0.2277)
56	Tb ³⁺	f^8	$ ^7F_5\rangle$	-0.9852	2	2036	7	-0.7299 (-0.7277)	-0.4962 (-0.5125)	0.7184 (0.7419)
57	Tb ³⁺	f^8	$ ^7F_4\rangle$	0.9781	3	3323	12	-0.1703 (-0.1528)	-0.5725 (-0.6075)	-0.7560 (-0.7650)
58	Tb ³⁺	f^8	$ ^7F_3\rangle$	-0.9763	4	4317	12	0.2068 (0.2277)	-0.1773 (-0.1880)	0.2150 (0.2129)
59	Tb ³⁺	f^8	$ ^7F_2\rangle$	-0.9745	5	5021	14	0.4186 (0.4382)	0.3839 (0.3984)	0 (0)
60	Tb ³⁺	f^8	$ ^7F_1\rangle$	0.9739	6	5487	10	0.5298 (0.5477)	0 (0)	0 (0)

Table 1 - cont.

No.	RE ion		Electron eigenstate data					Multipolar asphericity		
	Ion	conf.	Up.Comp.	Ampl.	no.	E	n	$A_2(\Psi)$	$A_4(\Psi)$	$A_6(\Psi)$
61	Tb ³⁺	f^8	$ ^7F_0\rangle$	0.9736	7	5717	7	0 (0)	0 (0)	0 (0)
62	Dy ³⁺	f^9	$ ^6H_{15/2}\rangle$	-0.9708	1	0	8	-1.5745 (-1.6095)	-0.9047 (-0.9134)	0.8503 (0.9000)
63	Dy ³⁺	f^9	$ ^6H_{13/2}\rangle$	-0.9830	2	3432	7	-1.2254 (-1.2375)	-0.3172 (-0.3128)	-0.3992 (-0.4146)
64	Dy ³⁺	f^9	$ ^6H_{11/2}\rangle$	-0.9577	3	5776	14	-0.9743 (-0.9587)	0.1970 (0.0108)	-0.2401 (-0.7152)
65	Dy ³⁺	f^9	$ ^6F_{11/2}\rangle$	0.9624	4	7377	11	0.4928 (0.4951)	-0.4364 (-0.2465)	-0.3538 (0.0853)
66	Dy ³⁺	f^9	$ ^6H_{9/2}\rangle$	-0.9685	5	7649	18	-0.7764 (-0.7786)	0.1267 (0.1423)	-0.6407 (-0.6845)
67	Dy ³⁺	f^9	$ ^6F_{9/2}\rangle$	0.9440	6	8731	16	0.2334 (0.2595)	0.1231 (0.1391)	-0.2286 (-0.2617)
68	Dy ³⁺	f^9	$ ^6H_{7/2}\rangle$	0.9653	7	9083	15	-0.7167 (-0.7176)	0.1037 (0.1129)	-0.6715 (-0.7035)
69	Dy ³⁺	f^9	$ ^6H_{5/2}\rangle$	0.9625	8	10149	12	-0.8418 (-0.8458)	-0.2803 (-0.2978)	0 (0)
70	Dy ³⁺	f^9	$ ^6F_{7/2}\rangle$	-0.9603	9	10626	22	0.0595 (0.0920)	0.1840 (0.2030)	0.2116 (0.2276)
71	Dy ³⁺	f^9	$ ^6F_{5/2}\rangle$	0.9653	10	12019	18	-0.0340 (-0.0130)	0.1464 (0.1260)	0 (0)
72	Dy ³⁺	f^9	$ ^6F_{3/2}\rangle$	0.9561	11	12818	17	-0.0502 (-0.0596)	0 (0)	0 (0)
73	Dy ³⁺	f^9	$ ^6F_{1/2}\rangle$	0.9570	12	13358	9	0 (0)	0 (0)	0 (0)
74	Ho ³⁺	f^{10}	$ ^5I_8\rangle$	0.9681	1	0	6	-0.6021 (-0.6562)	-0.6350 (-0.6797)	-1.6074 (-1.7060)
75	Ho ³⁺	f^{10}	$ ^5I_7\rangle$	0.9857	2	5066	6	-0.5324 (-0.5524)	-0.3942 (-0.4042)	-0.2371 (-0.2398)
76	Ho ³⁺	f^{10}	$ ^5I_6\rangle$	-0.9756	3	8613	11	-0.4943 (-0.4796)	-0.3011 (-0.2613)	0.2350 (0.3105)
77	Ho ³⁺	f^{10}	$ ^5I_5\rangle$	0.9492	4	11205	13	-0.4517 (-0.4428)	-0.2619 (-0.2437)	0.2542 (0.2958)
78	Ho ³⁺	f^{10}	$ ^5I_4\rangle$	-0.9472	5	13307	12	-0.4854 (-0.4540)	-0.4136 (-0.4103)	-0.7128 (-0.7679)
79	Ho ³⁺	f^{10}	$ ^5F_5\rangle$	0.9044	6	14747	12	0.5502 (0.7278)	-0.3680 (-0.3843)	0.0816 (0.1484)
80	Ho ³⁺	f^{10}	$ ^5S_2\rangle$	0.8429	7	17660	15	0.0188 (0)	0.0463 (0)	0 (0)

Table 1 - cont.

No.	RE ion		Electron eigenstate data					Multipolar asphericity		
	Ion	conf.	Up.Comp.	Ampl.	no.	E	n	$A_2(\Psi)$	$A_4(\Psi)$	$A_6(\Psi)$
81	Ho ³⁺	f^{10}	$ ^3L_9\rangle$	0.9462	21	28805	2	1.2573 (1.1349)	1.0060 (1.1236)	-0.6106 (-0.8368)
82	Er ³⁺	f^{11}	$ ^4I_{15/2}\rangle$	0.9852	1	0	3	0.6798 (0.6438)	0.6933 (0.6850)	1.7442 (1.7999)
83	Er ³⁺	f^{11}	$ ^4I_{13/2}\rangle$	0.9955	2	6514	3	0.5670 (0.5569)	0.4715 (0.4691)	0.6150 (0.6217)
84	Er ³⁺	f^{11}	$ ^4I_{11/2}\rangle$	0.9094	3	10170	5	0.3778 (0.5045)	0.2335 (0.3935)	0.2376 (0.3399)
85	Er ³⁺	f^{11}	$ ^4I_{9/2}\rangle$	0.6985	4	12286	7	0.0067 (0.4954)	0.3294 (0.4904)	0.5419 (1.1085)
86	Er ³⁺	f^{11}	$ ^4F_{9/2}\rangle$	0.7512	5	15038	7	-0.3421 (-0.7136)	0.3340 (0.4051)	0.1925 (-0.1799)
87	Er ³⁺	f^{11}	$ ^4S_{3/2}\rangle$	0.8293	6	18546	6	-0.1689 (0)	0 (0)	0 (0)
88	Er ³⁺	f^{11}	$ ^2H(2)_{11/2}\rangle$	0.6715	7	19185	5	0.0534 (0.0076)	-0.2887 (-0.5373)	0.4731 (-0.0066)
89	Er ³⁺	f^{11}	$ ^4F_{7/2}\rangle$	-0.9610	8	20192	7	-0.4633 (-0.4601)	-0.0505 (-0.0537)	0.4215 (0.4552)
90	Er ³⁺	f^{11}	$ ^4F_{5/2}\rangle$	-0.9254	9	21953	7	-0.3151 (-0.3220)	-0.1413 (-0.1890)	0 (0)
91	Er ³⁺	f^{11}	$ ^4F_{3/2}\rangle$	-0.7931	10	22316	4	-0.3403 (-0.3578)	0 (0)	0 (0)
92	Tm ³⁺	f^{12}	$ ^3H_6\rangle$	0.9956	1	0	2	1.5291 (1.5158)	0.9373 (0.9583)	-1.1246 (-1.1386)
93	Tm ³⁺	f^{12}	$ ^3F_4\rangle$	0.8028	2	5308	3	-0.1561 (-0.4672)	0.7045 (0.2906)	0.6365 (-0.1558)
94	Tm ³⁺	f^{12}	$ ^3H_5\rangle$	1	3	8192	1	1.3100 (1.3100)	0.6833 (0.6833)	-0.4451 (-0.4451)
95	Tm ³⁺	f^{12}	$ ^3H_4\rangle$	0.7688	4	12390	3	0.7100 (1.2367)	0.4743 (0.7395)	-0.9252 (-0.7706)
96	Tm ³⁺	f^{12}	$ ^3F_3\rangle$	1	5	13961	1	-0.3416 (-0.3416)	0.0627 (0.0627)	0.3193 (0.3193)
97	Tm ³⁺	f^{12}	$ ^3F_2\rangle$	0.8805	6	14659	3	-0.5151 (-0.3187)	-0.2386 (0.1328)	0 (0)
98	Tm ³⁺	f^{12}	$ ^1G_4\rangle$	0.7543	7	20957	3	0.5216 (0.3058)	1.0655 (1.2150)	0.8922 (1.5299)
99	Tm ³⁺	f^{12}	$ ^3P_2\rangle$	0.6938	8	27041	3	-0.6780 (-0.8366)	0.1478 (0)	0 (0)
100	Tm ³⁺	f^{12}	$ ^3P_0\rangle$	0.9714	9	33755	2	0 (0)	0 (0)	0 (0)

Table 1 - cont.

No.	RE ion		Electron eigenstate data					Multipolar asphericity		
	Ion	conf.	Up.Comp.	Ampl.	no.	E	n	$A_2(\Psi)$	$A_4(\Psi)$	$A_6(\Psi)$
101	Tm ³⁺	f^{12}	$ ^1I_6\rangle$	0.9956	10	34201	2	3.0185 (3.0318)	-1.4165 (-1.4375)	0.4414 (0.4554)
102	Tm ³⁺	f^{12}	$ ^3P_1\rangle$	1	11	34636	1	0.5477 (0.5477)	0 (0)	0 (0)
103	Tm ³⁺	f^{12}	$ ^3P_2\rangle$	-0.7047	12	37213	3	-0.9160 (-0.8366)	-0.5731 (0)	0 (0)
104	Yb ³⁺	f^{13}	$ ^2F_{7/2}\rangle$	1	1	0	1	1.3801 (1.3801)	-0.9670 (-0.9670)	0.3054 (0.3054)
105	Yb ³⁺	f^{13}	$ ^2F_{5/2}\rangle$	1	2	10450	1	1.1711 (1.1711)	-0.7560 (-0.7560)	0 (0)

Table 2: Multipole characteristics of the RE⁺³ ion eigenstates (selected from Table 1) distinguished by the strongest (the upper half) and the weakest (the lower half) $A = (A_2^2 + A_4^2 + A_6^2)^{1/2}$

No. in Table 1	RE ion	The upper state $^{2S+1}L_J$	A
13	Pr ³⁺	1I_6	3.3784
101	Tm ³⁺	1I_6	3.3634
5	Pr ³⁺	3H_6	2.1217
92	Tm ³⁺	3H_6	2.1169
18	Nd ³⁺	$^4I_{15/2}$	2.0160
41	Sm ³⁺	$^6H_{15/2}$	2.0159
62	Dy ³⁺	$^6H_{15/2}$	2.0051
82	Er ³⁺	$^4I_{15/2}$	1.9962
33	Pm ³⁺	5I_8	1.8909
74	Ho ³⁺	5I_8	1.8301
23	Nd ³⁺	$^4S_{3/2}$	0.0361
80	Ho ³⁺	5S_2	0.0500
72	Dy ³⁺	$^6F_{3/2}$	0.0502
42	Sm ³⁺	$^6F_{3/2}$	0.0565
43	Sm ³⁺	$^6F_{5/2}$	0.1068
71	Dy ³⁺	$^6F_{5/2}$	0.1503
87	Er ³⁺	$^4S_{3/2}$	0.1688
34	Pm ³⁺	5F_1	0.2180
25	Nd ³⁺	$^2H(2)_{11/2}$	0.2402
28	Nd ³⁺	$^2P_{3/2}$	0.2818

Table 3: Multipole characteristics of the RE⁺³ ion eigenstates (selected from Table 1) distinguished by the strongest $|A_k|$

No. in Table 1	RE ion	The upper state $^{2S+1}L_J$	A_2
13	Pr ³⁺	1I_6	-3.0273
101	Tm ³⁺	1I_6	3.0185
41	Sm ³⁺	$^6H_{15/2}$	1.5794
62	Dy ³⁺	$^6H_{15/2}$	-1.5745
92	Tm ³⁺	3H_6	1.5291
5	Pr ³⁺	3H_6	-1.5204
55	Tb ³⁺	7F_6	-1.5028
53	Eu ³⁺	7F_6	1.4991
2	Ce ³⁺	$^2F_{7/2}$	-1.3801
104	Yb ³⁺	$^2F_{7/2}$	1.3801
A_4			
13	Pr ³⁺	1I_6	1.4303
101	Tm ³⁺	1I_6	-1.4165
98	Tm ³⁺	1G_4	1.0665
2	Ce ³⁺	$^2F_{7/2}$	0.9670
104	Yb ³⁺	$^2F_{7/2}$	-0.9670
5	Pr ³⁺	3H_6	-0.9511
92	Tm ³⁺	3H_6	0.9373
9	Pr ³⁺	1G_4	-0.9275
41	Sm ³⁺	$^6H_{15/2}$	0.9086
62	Dy ³⁺	$^6H_{15/2}$	-0.9047
A_6			
18	Nd ³⁺	$^4I_{15/2}$	-1.7765
82	Er ³⁺	$^4I_{15/2}$	1.7442
33	Pm ³⁺	5I_8	1.6571
74	Ho ³⁺	5I_8	-1.6074
5	Pr ³⁺	3H_6	1.1338
92	Tm ³⁺	3H_6	-1.1246
15	Nd ³⁺	$^4I_{9/2}$	-1.0773
9	Pr ³⁺	1G_4	-1.0310
95	Tm ³⁺	3H_4	-0.9252
98	Tm ³⁺	1G_4	0.8922

Table 4: Multipole characteristics of the RE⁺³ ion eigenstates (selected from Table 1) distinguished by the weakest $|A_k|$

No. in Table 1	RE ion	The upper state $^{2S+1}L_J$	A_2
43	Sm ³⁺	$^6F_{5/2}$	0.0033
85	Er ³⁺	$^4I_{9/2}$	0.0067
80	Ho ³⁺	5S_2	0.0188
26	Nd ³⁺	$^4G_{5/2}$	0.0321
71	Dy ³⁺	$^6F_{5/2}$	-0.0340
23	Nd ³⁺	$^4S_{3/2}$	0.0362
9	Pr ³⁺	1G_4	-0.0421
72	Dy ³⁺	$^6F_{3/2}$	-0.0502
88	Er ³⁺	$^2H(2)_{11/2}$	0.0534
42	Sm ³⁺	$^6F_{3/2}$	0.0565
			A_4
25	Nd ³⁺	$^2H(2)_{11/2}$	0.0001
38	Sm ³⁺	$^6H_{11/2}$	-0.0042
80	Ho ³⁺	5S_2	0.0463
89	Er ³⁺	$^4F_{7/2}$	-0.0505
22	Nd ³⁺	$^4F_{7/2}$	0.0533
7	Pr ³⁺	3F_3	-0.0627
96	Tm ³⁺	3F_3	0.0627
21	Nd ³⁺	$^2H(2)_{9/2}$	-0.0638
6	Pr ³⁺	3F_2	-0.0909
45	Sm ³⁺	$^6F_{9/2}$	-0.1020
			A_6
46	Sm ³⁺	$^6F_{11/2}$	-0.0652
21	Nd ³⁺	$^2H(2)_{9/2}$	-0.0732
79	Ho ³⁺	5F_5	0.0816
24	Nd ³⁺	$^4F_{9/2}$	0.1040
86	Er ³⁺	$^4F_{9/2}$	0.1925
27	Nd ³⁺	$^4G_{7/2}$	0.1939
25	Nd ³⁺	$^2H(2)_{11/2}$	-0.2027
70	Dy ³⁺	$^6F_{7/2}$	0.2116
50	Eu ³⁺	7F_3	-0.2154
53	Eu ³⁺	7F_6	0.2161

Table 5: Multipole characteristics of the RE⁺³ ion eigenstates (selected from Table 1) distinguished by the largest $|A_k|/A$

No. in Table 1	RE ion	The upper state $^{2S+1}L_J$	A_2/A
14	Pr ³⁺	3P_2	0.9917
99	Tm ³⁺	3P_2	-0.9771
6	Pr ³⁺	3F_2	0.9659
35	Sm ³⁺	$^6H_{5/2}$	0.9538
64	Dy ³⁺	$^6H_{11/2}$	-0.9528
69	Dy ³⁺	$^6H_{5/2}$	-0.9488
21	Nd ³⁺	$^2H(2)_{9/2}$	0.9486
63	Dy ³⁺	$^6H_{13/2}$	-0.9233
39	Sm ³⁺	$^6H_{13/2}$	0.9227
90	Er ³⁺	$^4F_{5/2}$	-0.9124
			A_4/A
43	Sm ³⁺	$^6F_{5/2}$	-1.0000
26	Nd ³⁺	$^4G_{5/2}$	0.9977
71	Dy ³⁺	$^6F_{5/2}$	0.9731
80	Ho ³⁺	5S_2	0.9165
8	Pr ³⁺	3F_4	-0.8541
93	Tm ³⁺	3F_4	0.7322
98	Tm ³⁺	1G_4	0.7181
49	Eu ³⁺	7F_2	-0.6826
59	Tb ³⁺	7F_2	0.6759
9	Pr ³⁺	1G_4	-0.6685
			A_6/A
18	Nd ³⁺	$^4I_{15/2}$	-0.8812
74	Ho ³⁺	5I_8	-0.8783
33	Pm ³⁺	5I_8	0.8764
82	Er ³⁺	$^4I_{15/2}$	0.8737
85	Er ³⁺	$^4I_{9/2}$	0.8545
88	Er ³⁺	$^2H(2)_{11/2}$	0.8496
15	Nd ³⁺	$^4I_{9/2}$	-0.8485
25	Nd ³⁺	$^2H(2)_{11/2}$	-0.8440
57	Tb ³⁺	7F_4	-0.7846
51	Eu ³⁺	7F_4	0.7794

Table 6: Multipole characteristics of the RE⁺³ ion eigenstates (selected from Table 1) distinguished by the smallest $|A_k|/A$

No. in Table 1	RE ion	The upper state $^{2S+1}L_J$	A_2/A
85	Er ³⁺	$^4I_{9/2}$	0.0000
9	Pr ³⁺	1G_4	-0.0300
26	Nd ³⁺	$^4G_{5/2}$	0.0671
88	Er ³⁺	$^2H(2)_{11/2}$	0.0970
93	Tm ³⁺	3F_4	-0.1625
51	Eu ³⁺	7F_4	0.1664
57	Tb ³⁺	7F_4	-0.1766
70	Dy ³⁺	$^6F_{7/2}$	0.2064
71	Dy ³⁺	$^6F_{5/2}$	-0.2304
18	Nd ³⁺	$^4I_{9/2}$	-0.3268
			A_4/A
89	Er ³⁺	$^4F_{7/2}$	-0.0812
22	Nd ³⁺	$^4F_{7/2}$	-0.0837
68	Dy ³⁺	$^6H_{7/2}$	0.1054
66	Dy ³⁺	$^6H_{9/2}$	0.1249
14	Pr ³⁺	3P_2	0.1288
7	Pr ³⁺	3F_3	-0.1323
96	Tm ³⁺	3F_3	0.1323
37	Sm ³⁺	$^6H_{9/2}$	-0.1503
64	Dy ³⁺	$^6H_{11/2}$	0.1926
21	Nd ³⁺	$^2H(2)_{9/2}$	-0.2078
			A_6/A
46	Sm ³⁺	$^6F_{11/2}$	-0.1187
79	Ho ³⁺	5F_5	0.1229
53	Eu ³⁺	7F_6	0.1292
55	Tb ³⁺	7F_6	-0.1296
101	Tm ³⁺	1I_6	0.1311
13	Pr ³⁺	1I_6	-0.1334
24	Nd ³⁺	$^4F_{9/2}$	0.1578
2	Ce ³⁺	$^2F_{7/2}$	-0.1783
104	Yb ³⁺	$^2F_{7/2}$	0.1783
64	Dy ³⁺	$^6H_{11/2}$	-0.2347